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(71) Applicant
Coates Brothers PLC

(Incorporated in the United Kingdom)

Cray Avenue, St. Mary Cray, Orpington, Kent, BR5 3PP, United Kingdom

(72) Inventors
Nicholas Eric Ivory
Derek Edward Wilson
Michael Anthony Cockett

(74) Agent and/or Address for Service
Marks & Clerk
57-60 Lincoln's Inn Fields, London, WC2A 3LS, United Kingdom

(51) INT CL[5]
G03F 7/26, H05K 3/06

(52) UK CL (Edition K)
G2X XB20X
H1R RAE R12 R16 R18 R20

(56) Documents cited
GB 1537634 A GB 0585035 A EP 0154979 A2
US 4775611 A US 4645733 A US 4576900 A
US 4525448 A

(58) Field of search
UK CL (Edition J) G2C CRT3, G2X XB20X XND XNF
INT CL[4] G03C, G03F

(54) **Making metal patterns**

(57) A method of making a metal pattern by
(i) applying a layer of a radiation-curable material (2) to a substrate (1),
(ii) imagewise exposing the layer (2) to thereby cure exposed portions of the layer (2a)
(iii) removing the unexposed portions (2b)
(iv) applying a metal layer (4) then a second layer of radiation curable material and image-wise exposing to the negative used in step (ii),
(v) removing the unexposed portions (5a) and the underlying metal
(vi) removing the exposed portions (5b) and depositing the same or another metal (4') on metal pattern (4) surrounded by cured resist (2a).

Alternatively, in step (iv) the same original as in step (ii) may be used, the unexposed areas removed and the same or another metal electroplated on exposed metal pattern and cured second resist and underlying metal removed to produce a metal pattern (Fig 2 not shown).

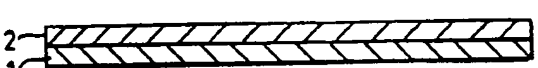



FIG.1b.

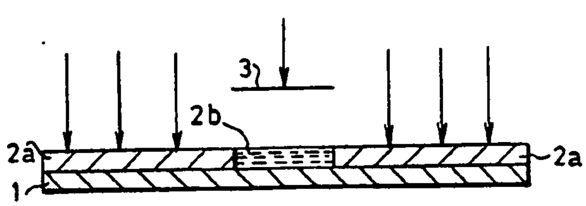



FIG.1c.

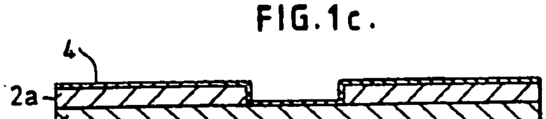



FIG.1d.

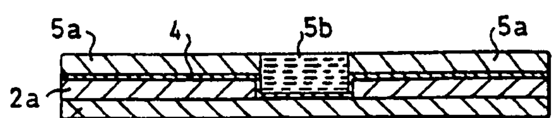



FIG.1e.

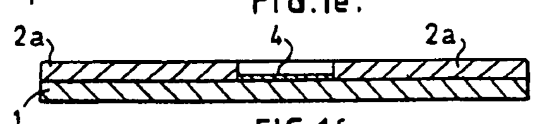



FIG.1f.

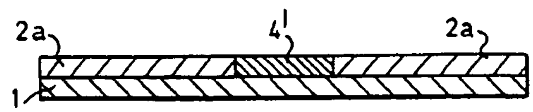



FIG.1g.

The references to figures(s) 7e-7f of the drawings in the printed specification are to be treated as omitted under Section 15(2) or (3) of the Patents Act 1977.

GB 2 230 871 A


FIG.1a.


FIG.1b.

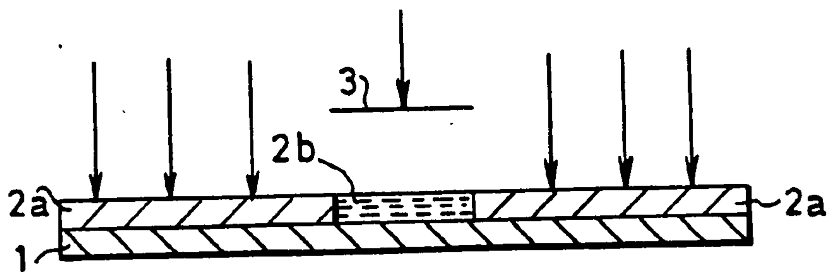



FIG.1c.

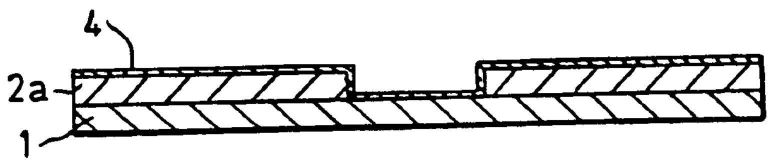



FIG.1d.

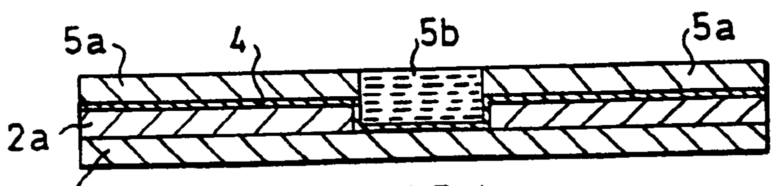



FIG.1e.

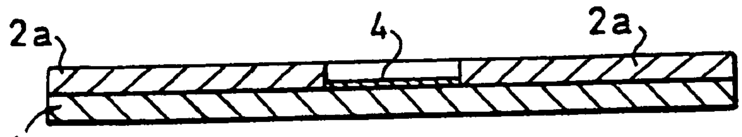



FIG.1f.

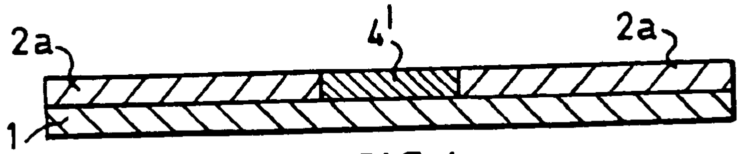



FIG.1g.

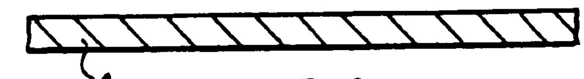



FIG.2a.

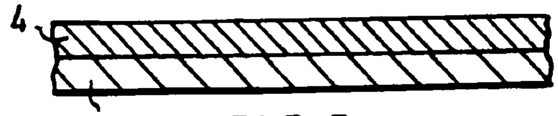



FIG.3a.

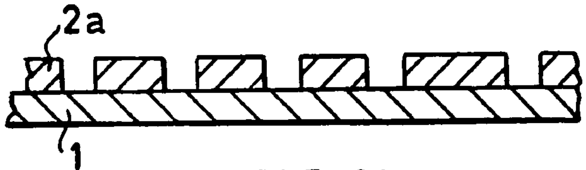



FIG.2b.

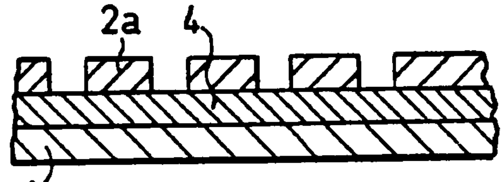



FIG.3b.

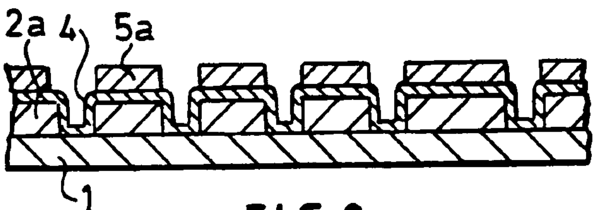



FIG.2c.

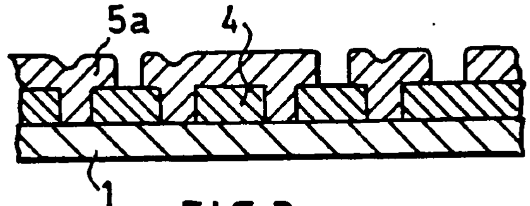



FIG.3c.

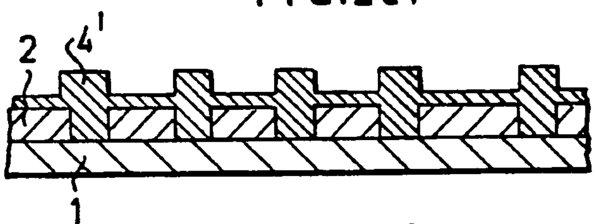



FIG.2d.

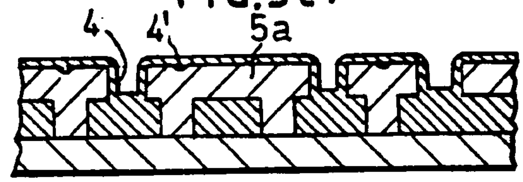



FIG 3d.

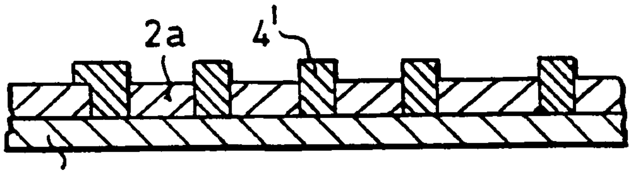



FIG.2e.

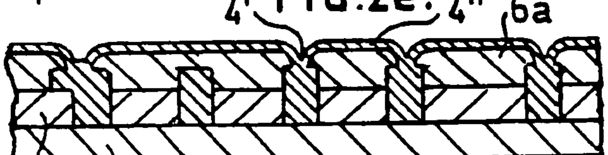



FIG.2f.

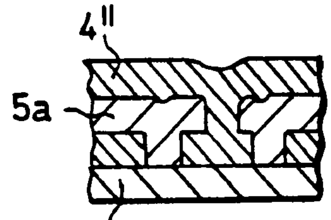



FIG.3e.

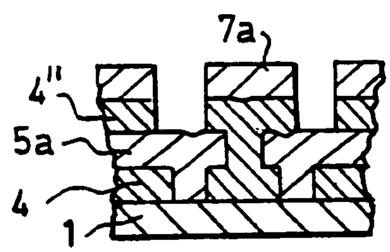
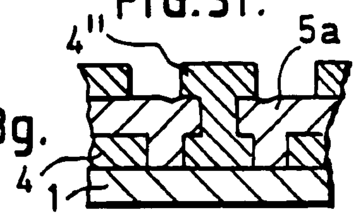



FIG.3f.

FIG.3g.



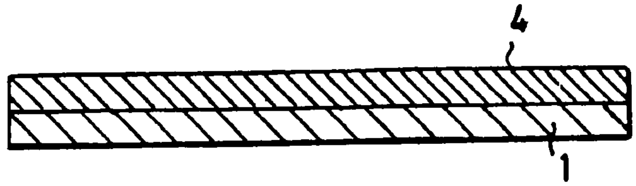


FIG.4a.

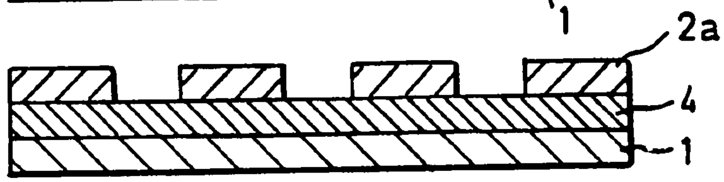


FIG.4b.

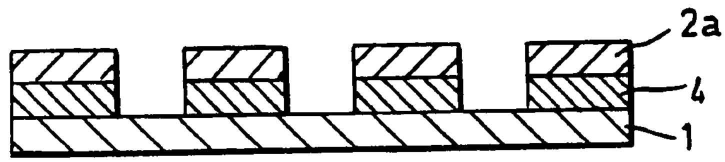


FIG.4c.

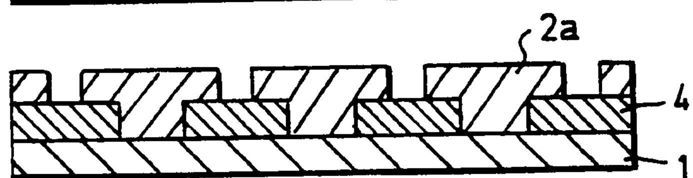


FIG.4d.

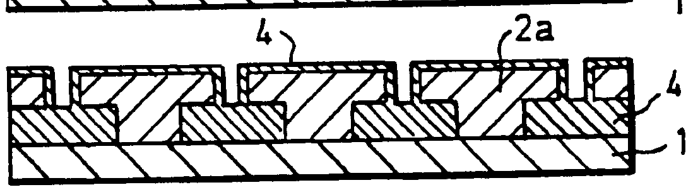


FIG.4e.

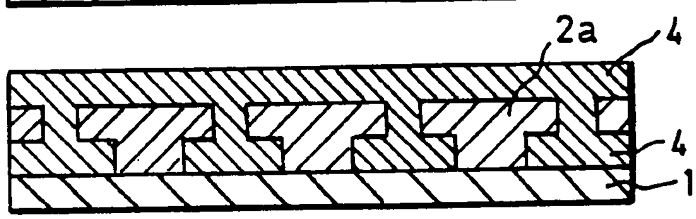


FIG.4f.

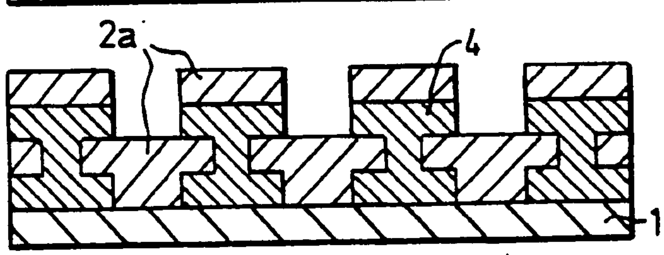


FIG.4g.

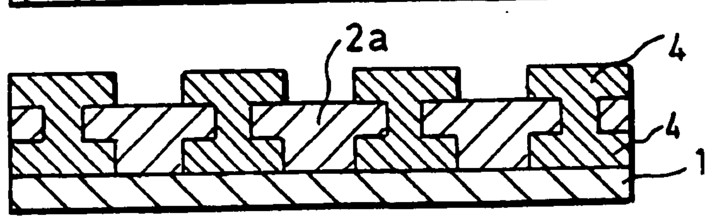


FIG.4h.

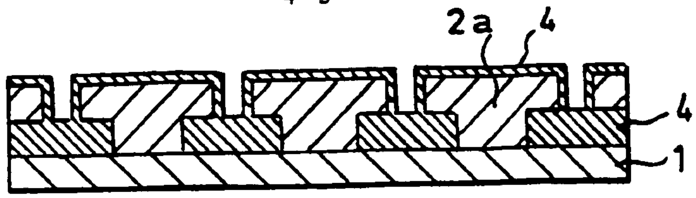


FIG.5a.

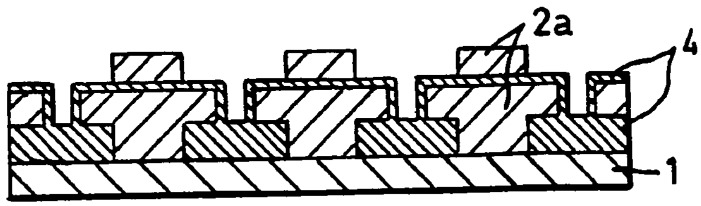


FIG.5b.

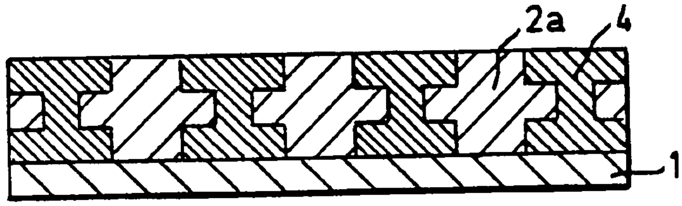


FIG.5c.

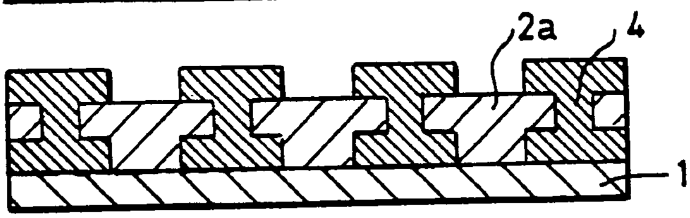


FIG.5d.

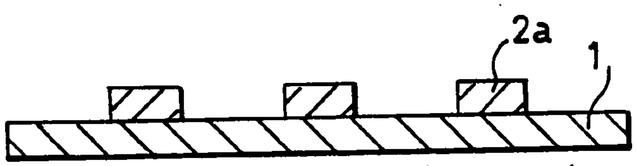


FIG.6a.

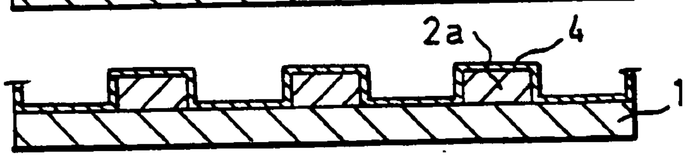


FIG.6b.

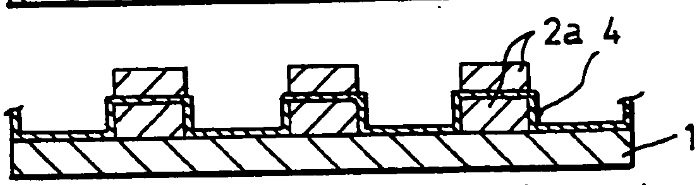


FIG.6c.

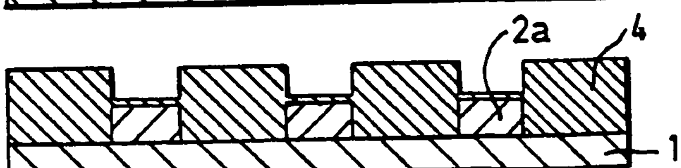


FIG.6d.

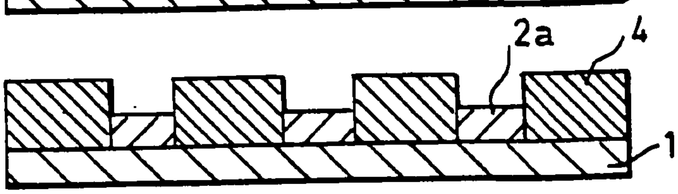


FIG.6f.

FIG 7a

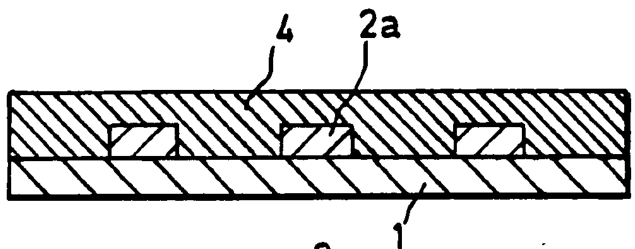



FIG.7b.

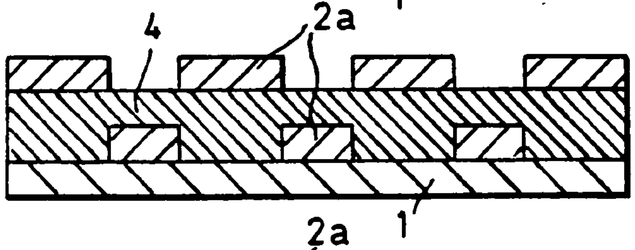



FIG.7c.

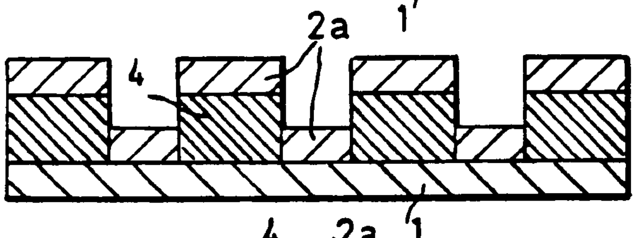
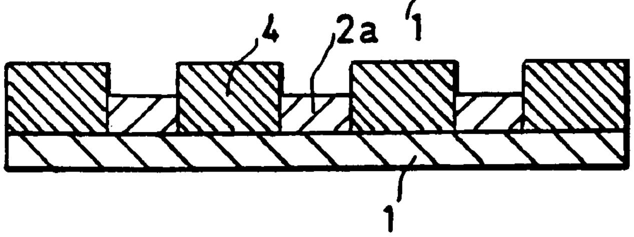



FIG.7d.



Printed Circuit Boards

This invention is concerned with improvements and relating to the manufacture of printed circuit boards and the like. Thus, the present invention relates to the manufacture of patterned layers of electrically conductive metals on electrically insulating substrates and is particularly concerned with a method of their manufacture which lends itself to the production of multilevel circuit boards, that is boards having a layered stack of circuits, each insulated from the other but interconnected as and where appropriate.

The use of so-called "resists" in the manufacture of printed circuit boards and the like is well established, and, thus, photo-definable resists are widely used to produce masks for operations such as etching, plating and soldering. The present invention employs photo-definable resists and is, among other things, characterised in that the cured resists, at least to some extent, form part of the final product.

Basically the present invention provides a method of making an insulated patterned layer of an electrically conductive metal on a substrate including the steps of

forming a patterned relief layer of an electrically insulating resist material upon the substrate, by a photodefinition process, and then introducing electrically conductive metal into the depressions (tracks) in the patterned relief layer.

The photodefinition process used to form the patterned relief layer is one comprising the stages of:

(i) applying a layer of a radiation-curable material to the substrate;

(ii) imagewise exposing the layer of radiation-curable material to radiation to thereby cure portions of the layer exposed to such radiation; and

(iii) removing portions of the layer not exposed to radiation by means of a suitable solvent to thereby produce upon the substrate a patterned layer of cured radiation-curable material.

Conductive metal may be introduced into the tracks in the patterned relief layer in any desired way but is conveniently be introduced by forming a thin layer of conductive metal in the tracks and then introducing further metal into the tracks by an electroless or electrolytic deposition process. The thin layer of conductive metal will generally be formed over the whole

surface of the patterned relief layer including upstanding portions thereof as well as the tracks between the upstanding portions. To avoid plating of metal on to the upstanding parts these may first be stripped of their metal whilst protecting the layer of conductive metal in the tracks. Alternatively the whole of surface of the patterned layer may be plated so that the thickness of metal in the track portions is greater than that on the upstanding portions, and excess metal then etched from the whole to strip the upstanding portions whilst leaving metal in the track portions.

In accordance with a particular embodiment of the invention, the metal is introduced by the further steps of:-

(iv) applying a layer of electrically conductive metal over the surface of the substrate and relief patterned cured material obtained in step (iii) of the photodefinition process;

(v) applying a layer of a radiation-curable material over the surface of the layer of metal deposited in step (iv);

(vi) imagewise exposing the layer of radiation-curable material to radiation in a pattern the negative of that used in step (ii) of the photodefinition process whereby to cure portions of the radiation-curable material exposed to such radiation, but to a lesser extent than the patterned cured material already present on the substrate;

(vii) removing unexposed portions of the radiation-curable material by means of an appropriate solvent to expose portions of the metal layer obtained in step (iv);

(viii) removing the portions of metal exposed in step (vii) by means of an appropriate etchant;

(ix) removing the cured material obtained in step (vi) to thereby expose other portions of metal deposited in step (iv); and

(x) depositing additional electrically conductive metal upon the patterned metal portions exposed in step (ix).

In accordance with another embodiment of the invention the metal is introduced into the tracks by the steps of:-

(iva) applying a layer of electrically conductive metal over the surface of the substrate and relief patterned cured material obtained in step (iii) of the photodefinition process;

(va) plating a coating of electrically conductive metal over thewhole surface of the layer of metal applied in step (iva); and

(via) etching the metal coating applied in step (va) to remove metal from upstanding parts of the relief pattern whilst leaving metal in the tracks between the upstanding portions.

In accordance with a yet further embodiment of the invention metal is introduced into the tracks by the steps of:

(ivb) applying a layer of electrically conductive metal over the surface of the substrate and relief patterned cured material obtained in step (iii) of the photodefinition process;

(vb) applying a layer of radiation-curable material over the surface of the layer of metal deposited in step (ivb);

(vib) imagewise exposing the layer of radiation-curable material to radiation in the pattern used in step (ii) of the photodefinition process whereby to cure portions of the radiation-curable material exposed to radiation;

(viib) removing unexposed portions of the radiation- curable material applied in step (vb) to expose portions of metal applied in step (ivb);

(viiib) plating electrically conductive metal onto the portions of metal exposed in step (viib);

(ixb) removing the cured material obtained in step (viib) to expose further portions of metal applied in step (ivb); and

(xb) etching any of the portions of metal exposed in step (ixb).

The overall general process of the invention is preferably repeated a number of times to build up a series of layers, one overlying the other. If desired, intermediate layers of photocured resist material may be applied to each of the layers applied as described above and such intermediate layers will generally have through holes (which will be formed by a photodefinition process) appropriately connected to connect the tracks in one layer to those in another. Metal may be introuced into such through holes as and when introducing metal into the tracks in a patterned relief layer immediately above the intermediate layer. Final connections may also be made by applying a layer of metal over the surface of a patterned board.

The first layer of a series of layers of the invention may be formed upon an electrically insulating substrate or may be formed upon a substrate bearing a layer of electrically conductive metal, to facilitate subsequent plating of the tracks in the first patterned relief layer.

In order that the invention may be well understood reference will be made to the accompanying drawings which are simplied schematic cross-sections through boards illustrating various stages in processes according to the invention; Figs. 1(a) - 1(g), 2(a) - 2(f) and 3(a) - 3(g) illustrating general processes of the invention, and Figures 4(a) - 4(h), 5(a) - 5(d), 6(a) - 6(e) and 7(a) - 7(f) illustrating particular processes as described in the Examples below.

The starting basis for the process illustrated in Figs. 1(a) -1(g) is an insulating substrate, 1 [see Fig. 1(a)]. This will commonly be, as is general in the printed circuit board art, a sheet of reinforced plastics material such a phenolic or epoxy laminate.

In step (i) of the process, there is applied to the insulating substrate, 1, a layer, 2, of a radiation-curable material [see Figure 1 (b)]. The radiation-curable material will, most conveniently, be a UV-curable material and to this extent will contain, as a constituent component, a photo-sensitiser or photoinitiater. Such catalysts are well known in the field of UV-curable compositions and typical examples are dimethoxy phenyl acetophenone, benzophenone and 4,4'-bis(dimethylamine) benzophenone.

The curable component of the curable composition will generally be an ethylenically unsaturated material, especially one containing terminal ethylenically unsaturated groups. A wide variety of materials is known and has been proposed for use in radiation-curable compositions and typical examples thereof include esters of ethylenically unsaturated carboxylic acids (typically acrylic or methacrylic acid) and esters of ethylenically unsaturated alcohols (such as allyl alcohol). Particularly suitable ethylenically unsaturated materials are polyethylenically unsaturated materials obtained by the reaction of ethylenically unsaturated carboxylic acids with saturated materials containing groups reactive with the carboxyl groups of such acids, especially epoxy resins such as epichlorohydrin/Bisphenol A epoxy resins or epoxy Novolak resins. In addition to the ethylenically unsaturated component and UV-photosensitizer the curable compositions may contain other ingredients such as so-called "solder resists" or colouring agents, fillers etc. It is particularly preferred, in accordance with the invention, to use curable compositions containing relatively large amounts of inert fillers, especially those such as are disclosed in our GB-B-2032939 and sold under the trade name "Imagecure". Such compositions comprise unsaturated material, photoinitiator and filler together with a volatile organic solvent and after

application to a substrate the solvent is allowed to evaporate off to form a substantially non-tacky film of curable material thereon.

In accordance with an especially preferred embodiment of the invention, the curable composition is one which is developable (see the discussion below) with aqueous alkaline systems and to this end the ethylenically unsaturated material suitably contains free carboxyl groups to permit of solubility in aqueous alkaline solutions. Thus, a particularly preferred form of ethylenically unsaturated material for use in the curable composition is a reaction product of an ethylenically unsaturated carboxylic acid with an epoxy resin, which reaction product has later been modified by reaction with an anhydride of a dicarboxylic acid, to introduce free carboxyl groups into the resultant material.

In step (ii) of the process, substrate 1 bearing the layer of curable material 2 is exposed to radiation (typically UV radiation) as schematically shown in Fig. 1(c) of the drawings. As a result of this irradiation, portions, 2a, of the curable material exposed to the radiation are cured whereas those, 2b, not so exposed remain uncured. It is important that the cured material, 2a, obtained should be more strongly cured or

cross-linked than that obtained in subsequent step (vi) and this may be achieved by employing, in step (ii) a higher radiation dose (e.g. a longer period of radiation) than in subsequent step (vi). The degree of cure of the material 2a may also be increased by heating it, e.g. at temperatures of 100 to 150° for periods of 15 to 120 minutes.

In step (iii), the irradiated curable material is "developed", that is the uncured portions 2b, are removed by dissolution with an appropriate solvent. Suitable solvent systems include, for the preferred alkali-developable materials noted above, aqueous alkali solutions such as dilute solutions of sodium hydroxide or sodium carbonate. On the other hand, organic solvent developers may be employed and examples of such suitable solvents include glycol ethers, particularly diethylene glycol monobutyl ether; ketones or aromatic hydrocarbons.

In step (iv), a layer, 4, of electrically conductive metal is applied to the substrate bearing the cured/developed radiation-curable material to give a board as illustrated in Figure 1(d) of the drawings. The metal is most conveniently applied by a vapour deposition method and may be any suitable electrically-conductive metal. Typically, copper will be preferred but, of course, other conductive metals such as aluminium, silver etc. may be employed.

The layer of electrically conductive material applied in this step should generally be thin, e.g. from 0.5 to 10, preferably 1 to 5 microns in thickness. In steps (v) and (vi) a further layer of radiation-curable material, 5, is supplied over the surface of the layer of metal, 4, and this is then imagewise exposed to radiation, in a pattern the negative of that used in step (ii); as schematically illustrated in Figure 1(e) of the drawings. As a result irradiated portions of this second layer of photocurable material are cured (but to a lesser extent than the portions, 2a, of the original radiation-curable material) and unirradiated portions are not cured.

In step (vii) the layer, 5a, 5b, of irradiated photo- curable material is developed, in a manner similar to that discussed in connection with step (iii) above. Exposed portions of the metal layer 4 thus revealed, i.e. those originally under unirradiated portions 5a of the second layer, 5, of photo-curable material, are removed with a suitable etchant.

As a result there is obtained a board as schematically illustrated in Figure 1(f) of the drawings, that is one containing a layer of electrically- conductive metal only in those portions, tracks, between the originally formed patterned layer of

cured material 2a. In the final step, further electrically conductive material, 4', is introduced into the portions or tracks between the patterned parts 2a and covering the original layer 4 of electrically conductive material. This additional material may be the same or a different metal from that forming original thin layer 4. The layer 4' may be formed by any suitable method for forming a layer of an electrically conductive material on an already present patterned layer of electrically conductive metal e.g. by electroplating or, more preferably, by electroless plating. Compositions and methods suitable for electroplating or electroless deposition of electrically conductive metals on thin layers of electrically conductive metals are well known in the printed circuit board art and are described, for example, in "Printed Circuit Handbook", C.F. Coombs, 2nd Edition, McGraw-Hill, 1979.

As shown in Fig. (g) the thickness of the conductive layer 4' is substantially the same as that of the layer of insulating material 2a, formed from the original radiation-curable material. The use of this order of thickness readily facilitates the build-up, repeatingly using the method of the invention, of multilayer or multi-level printed circuit boards; each such subsequent layer being formed by repeating steps (i) - (x) detailed

above. Interconnection between successive layers may readily be achieved by appropriate patterning of the tracks 4' of conductive material in each layer so that, where appropriate, one conductive tract crosses, and connects with, a track in a layer immediately below.

Alternatively, as discussed above, intermediate layers of cured material having appropriately positioned holes may be used to build up multi-level beds using the process of the invention.

The process generally illustrated in Figures 2(a) - 2(f) of the drawings also starts from the basis of an insulating laminate 1 as shown in Figure 2(a). A curable resist is applied to the surface of the laminate and photoimaged to give a patterned relief layer of cured resist, 2(a), supported on laminate 1, as shown in Figure 2(b). A thin layer of conductive metal (hereinafter simply "copper", 4, is then deposited over the patterned relief layer and a further patterned layer of cured resist material, 5(a), is formed over the copper layer by photodefinition and development to give the product shown in Figure 2(c). Copper is then electroplated into the spaces between the corresponding tracks of resist layers 2(a) and 5(a) and, subsequently, resist portions 5(a) are stripped to leave a patterned layer of copper, 4', and cured resist, 2(a), supported

on laminate 1 as shown in Figure 2(d). Excess copper is then removed or etched to leave the arrangement shown in Figure 2(e), namely one comprising individual copper tracks, 4', separated by insulating portions of cured resist 2(a). Finally, a further patterned layer of cured resist, 6(a), is applied to the surface of the copper and resist and then this is plated over with copper, 4'', to give the arrangement shown in Figure 2(f) comprising tracks of copper, 4', insulated by cured resist material, 2(a), 6(a) and connected, as desired, by copper layer 4''.

The process illustrated in Figures 3(a) - 3(g) of the drawings starts from a laminate board, 1, bearing a layer of copper 4, as shown in Figure 3(a). A patterned relief layer of cured resist, 2(a) is applied to the surface of the copper, as shown in Figure 3(b), unprotected portions of copper are etched away, and then a further layer of cured resist, 5(a), is applied to the patterned copper layer, as shown in Figure 3(c). A thin layer of copper, 4', is then applied over the surface of cured resist 5(a) [see Figure 3(d)] and is then electroplated with copper 4'' [see Figure 3(e)]. The layer of copper 4'' is then given a further coating of patterned cured resist material, 7(a), and unprotected portions of the copper layer 4'' are etched away. [See Figure 3(f)]. Finally cured resist 7(a) is removed to

give the arrangement shown in Figure 3(g). The individual copper tracks shown in this arrangement may, if desired, be interconnected as discussed above in connection with Figure 2(f).

In order that the invention may be well understood the following examples are given by way of illustraton only.

In the examples reference will be made to Figures 4(a) - 4(h), 5(a) - 5(d), 6(a) - 6(e) and 7(a) - 7(f) of the drawings. In all these Figures numeral 1 refers to an insulating laminate, numeral 4 refers to copper and numberal 2a to cured resist material.

Example 1

One ounce (35 micron) copper foil on FR 4 laminate board [Figure 4(a)] was coated, to a dry film thickness of 25 microns, with a layer of a photocurable, alkali-developable resist material sold under the Trade Name Imagecure XV 501. The board was then irradiated with ultraviolet light through a patterned mask so that the coating over the desired circuit pattern was hardened by the irradiation. The unexposed coating material was then washed from the board using 0.6% by weight of carbonate solution to give a patterned relief image of

cured resist over the copper [Figure 4(b)]. The areas of copper not protected by the resist were then etched away using an acid ferric chloride etchant [Figure 4(c)] and the layer of resist remaining over the unetched compound was removed by dipping the board in 3% by weight sodium hydroxide solution. Another layer of Imagecure XV 501 was then coated over the board to a dry film thickness of 30 microns. This layer of resist was photoimaged using a mask suitable for the production of interlayer connections and developed as described above and was then heat and UV cured to a give a hard curable coating [Figure 4(d)]. The board was then plasma etched and given an all-over coat of copper metal (1 - 2 microns thick) by vacuum sputtering [Figure 4(e)]. The board was then plated all over (panel plated) by an electrolytic method to give a layer of copper 15 microns thick all over the board [Figure 4(f)]. Another layer of Imagecure XV 501 (about 25 microns dry film thickness) was then put down over the board and photoimaged through an appropriate etch resist mask. The board was then developed and the copper exposed by this development was etched away using the ferric chloride etchant [Figure 4(g)]. The resist remaining on the newly produced circuit pattern was removed using 3% by weight sodium hydroxide solution. The layer of cured resist laid down before the metallisation was unaffected by this stripping process because of its greater degree of cure [Figure 4(h)].

Example 2

The procedure of Example 1 was repeated upto the stage illustrated in Figure 4(e) [Figure 5(a)]. A further layer of imagecure was then laid down over the thin layer of vacuum deposited copper and photoimaged through an appropriate pattern. The uncured areas of the film were developed away as in Example 1 [Figure 5(b)] and the exposed areas of copper were electroplated to the desired thickness of 20 microns [Figure 5(c)]. The resist was then stripped with 3% by weight sodium hydroxide solution and the remaining thin layer of vacuum deposited copper was flash etched off using acid ferric chloride solution [Figure 5(d)].

Example 3

An SR 4 plain laminate board was coated with Imagecure XV 501 at a dry film thickness of 25 microns. The board was imagewise exposed through a patterned mask so that the resist over the desired circuit patterned remained unharmed. The board was then developed in 0.6% by weight sodium carbonate solution [Fig.6(a)] and the resist layer remaining was then fully heat and UV cured. The board was then plasma etched and given an all-overcoat of metallic copper, 1 micron thick, by vacuum sputtering [Figure 6(b)]. Another layer of

resist was then deposited over the metal surface and photoimaged through the mask used to image the previous layer and this was then developed as before [Figure 6(c)]. The board was then pattern electroplated and the resist stripped using 3% by weight sodium hydroxide solution [Figure 6(d)]. The layer of vacuum deposited copper but not built up by the electroplating was then flash etched using acid ferric chloride solution.

Example 4

The procedure of Example 3 was repeated up to the stage shown in Figure 6(b). A layer of copper (20 microns thick) was then electroplated over the surface of the thin layer of copper. [Figure 7(a)]. A layer of Imagecure XV 501 (about 25 microns dry thickness) was then deposited on to the board and photoimaged through a mask that was the negative of that used in the formation of the initial resist layer. This layer was developed as before [Figure 7(b)] and the copper exposed by this process was then etched away using acid ferric chloride etchant [Figure 7(c)]. The resist over the copper tracks remaining was then stripped away using 3% sodium hyroxide solution [Figure 7(d)].

CLAIMS

1. A method of making an insulated patterned layer of an electrically conductive metal upon a substrate including the steps of forming a patterned relief layer of an electrically insulating resist material upon the substrate by a photodefinition process comprising the steps of:

(i) applying a layer of a radiation-curable material to the substrate;

(ii) imagewise exposing the layer of radiation-curable material to radiation to thereby cure portions of the layer exposed to such radiation; and

(iii) removing the portions of the layer not exposed to radiation by means of a suitable solvent to thereby produce upon the substrate a patterned layer of cured radiation-curable material; and

subsequently introducing electrically conductive metal into the depressions (tracks) in the patterned relief layer.

2. A method as claimed in claim 1 in which the metal is introduced into the tracks by the further steps of:

(iv) applying a layer of electrically conductive metal over the surface of the substrate and relief pattern cured material obtained in step (iii) of the photodefinition process;

(v) applying a layer of a radiation-curable material over the surface of the layer of metal deposited in step (iv);

(vi) imagewise exposing the layer of radiation-curable material to radiation in a pattern the negative of that used in step (ii) of the photodefinition process where the cured portions of the radiation-curable material exposed to such radiation, but to a lesser extent than the patterned cured material already present on the substrate;

(vii) removing the unexposed portions of the radiation-curable material by means of an appropriate solvent to expose portions of the metal layer obtained in step (iv);

(viii) removing the portions of metal exposed in step (vii) by means of an appropriate etchant;

(ix) removing the cured material obtained in step (vi) to thereby expose other portions of metal deposited in step (iv); and

(x) depositing additional electrically conductive metal upon the patterned metal portions exposed in step (ix).

3. A method as claimed in claim 1 in which the metal is introduced into the tracks by the steps of:

(iva) applying a layer of electrically conductive metal over the surface of the substrate and relief patterned cured material obtained in step (iii) of the photodefinition process;

(va) plating a coating of electrically conductive metal over the whole surface of the layer of metal obtained in step (iva); and

(via) etching the metal coating obtained in step (va) to remove metal from upstanding areas of the relief pattern while leaving metal in the depressions between the upstanding areas.

4. A method as claimed in claim 1 in which themetal is introduced into the tracks by the steps of:-

(ivb) applying a layer of electrically conductive metal over the surface of the substrate and relief patterned cured material obtained in step (iii) of the photodefinition process;

(vb) applying a layer of radiation-curable material over the surface of the layer of metal deposited in step (ivb);

(vib) imagewise exposing the layer of radiation-curable material to radiation in the pattern used in step (ii) of the photodefinition process whereby to cure portions of the radiation-curable material exposed to radiation;

(viib) removing unexposed portions of the radiation- curable material applied in step (vb) to expose portions of metal applied in step (ivb);

(viiib) plating electrically conductive metal onto the portions of metal exposed in step (viib);

(ixb) removing the cured material obtained in step (viib) to expose further portions of metal applied in step (ivb); and

(xb) etching any of the portions of metal exposed in step (ixb).

5. A process as claimed in claim 1 substantially as hereinbefore described with reference to the accompanying drawings.

6. A process as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

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